②

ELECTRONIC AND OPTICAL PROPERTIES OF SbSBr, SbSI AND SbSeI[*]

J.F. Alward and C.Y. Fong[†]

Department of Physics

University of California

Davis, CA 95616

and

M. El-Batanouny and F. Wooten

Department of Applied Science

University of California

Davis, CA 95616

October 3, 1977

D D C

RECEIVED

MAR 31 1978

B

ABSTRACT

Electronic band structures of the ternary semiconductors SbSBr and SbSeI have been obtained by using the empirical pseudopotential method (EPM) to fit our measured optical reflectivity data and earlier gap measurements. An SbSI band structure has been determined by fitting to earlier reflectivity and Raman spectroscopic data, and the results agree better with the data than do the results of an earlier preliminary EPM calculation. Above the SbSI conduction band minimum are secondary minima located midway along the ΓZ and ΓX symmetry lines. These minima may in part be responsible for the observed microwave oscillation (Gunn effect) in this crystal. Similar minima in SbSBr and SbSeI are reported, suggesting these crystals might also show microwave properties. The total densities of states are presented.

The ternary semiconductors SbSBr, SbSI and SbSeI have attracted considerable attention in recent years, in part because of observed phase transitions,[1] anisotropy,[2] piezoelectric behavior,[3] nonlinear optical behavior[4] and photoconductivity.[5] Furthermore, microwave oscillation (the Gunn effect) has also been observed in SbSI.[6] The purpose of the present communication is to report the electronic and optical properties of these crystals.

Details of the growth, sample preparation and room-temperature reflectance measurements will be presented in a more detailed later publication.

The empirical pseudopotential method (EPM) has already been discussed in detail elsewhere.[7] The essence of the EPM is that the potentials of the constituent atoms are expanded in plane waves. The coefficients of these expansions are empirically adjusted to fit the experimental results. Additional details pertinent to the specific application of the EPM to the present orthorhombic crystals is given in a previously reported EPM calculation for SbSI by Fong et al.[8] The lattice constants and atomic locations are given in Wyckoff.[9]

The theoretical and experimental optical reflectivity spectra are shown in Fig. 1. The measured SbSI spectra reported by Fong et al[8] are for polarizations parallel and perpendicular to the shortest crystal axis. The present SbSBr and SbSeI measurements are unpolarized.

The theoretical reflectivity agreement with the SbSI data is generally better than that obtained in the calculation by Fong et al[8] (not shown). In the present results, the potential associated with

the Sb atom is about 0.03 rydberg less attractive on the average
than in their results, so there is greater transfer of charge from
the Sb to the S and I atoms. The present I and S potentials are
nearly the same as the earlier calculation. The main improvement
over the earlier calculation is in the shape of the structure near
2 eV in the parallel-polarized reflectivity. In the earlier result[8]
the theoretical structure is a smooth, rounded peak, while the present
peak shows the same type of sub-structure as in the data: a shoulder
about 0.1 eV below a sharp peak at 2 eV. The appearance of these two
separate structures, instead of the single rounded peak found by Fong
et al[8], is associated with the increased separation of unoccupied S
and Sb states caused by the elevation of the Sb potential. For the
perpendicular polarization, the main improvements over the earlier
results[8] is in the location of the lowest peak, which is about 0.25 eV
too low in their results. In the present results, the location of this
peak agrees to 0.05 eV with the measured location.

The measured spectra of SbSBr and SbSeI each show three main
structures. Each of the theoretical spectra also show three structures
and the locations of these structures agree to the order of 0.2 eV
with the locations in the data. The largest discrepency between the
results is found in the heights of the lowest-energy structure near
2.5 eV in SbSBr. The strong peak at 2.37 eV in the data finds
correspondence to only a weak shoulder at 2.55 eV in the theory.

A common feature of the theoretical and experimental spectra is
the location of either a peak or a shoulder within 0.5 eV above the
threshold of optical transitions. These structures also share a

common origin: about 70% of the strength of each structure arises from transitions from chalcogenide sp states in the top valence band to antimony sp states in the bottom conduction band. The remaining peaks in the various spectra do not share well-defined common origins; details regarding their specific origins are available on request.

Since the locations of the theoretical peaks agree to the order of 0.2 eV with the experimental locations, the relative locations of the energy bands are probably also accurate to the order of 0.2 eV. These energy bands are shown in Fig. 2. Because the band structures were obtained by fitting to only the optical energy range of the reflectivity data, we may regard as accurate only those bands for which the valence-to-conduction band separations are in the optical energy range. These are the only bands shown in Fig. 2.

In the SbSBr band structure, the valence band maximum is slightly displaced from the usual location of the maximum (at Γ) in semiconductors. However, this maximum is only 0.05 eV above the energy at Γ. Since the uncertainty in the present energy bands is of the order of 0.2 eV, these results cannot rule out the possibility that the actual valence band maximum is at Γ. The conduction band minimum for SbSBr is at the S symmetry point. The fundamental gap is thus indirect, with a value 2.18 eV. This is in excellent agreement with the gap (2.22 eV) reported by Pikka and Fridkin.[10]

In SbSI, the gap is 2.11 eV and is indirect, from Γ to S. Recent Raman spectroscopic measurements by Shen[11] yielded values of 2.05 eV and 2.20 eV for perpendicular and parallel polarizations, respectively. The average of these measurements, 2.12 eV, is in

- 5 -

excellent agreement with the theory. The data[11] indicates that the
gap is <u>direct</u>, but since the uncertainty in the bands is about 0.2 eV,
the present results should not be regarded as inconsistent with the
data. Indeed, the smallest direct gap (2.28 eV), at the S symmetry
point, is only 0.17 eV larger than the indirect gap, suggesting that
the gap measured by Shen[11] may have been at S.

In SbSeI, the gap is 1.67 eV and is also indirect, from Γ to S.
This is in good agreement with the data (1.71 eV) reported by Pikka
and Fridkin.[10] The gap, however, is significantly smaller than in
SbSBr and SbSI. The reason for this difference is discussed below.

Among all of the constituent atoms Sb, S, Se, I and Br, the
Sb atom is the least electronegative. (Thus, the lowest unoccupied
states would originate from the Sb sp states from which an electron has
been transferred to the halide.) On the other hand, since the
halides are the most electronegative, the occupied sp states of I or
Br are expected to lie the farthest below the top of the valence bands.
The largest portion of the occupied states at the gap must therefore
come from the sp states of the chalcogenides and the remaining states
of Sb.[12] Compared to Se, the S atoms are more electronegative.
Therefore, the bonds between S and Sb should be more ionic than the
ones between Se and Sb. Consequently, the gaps in the former crystals
(SbSBr and SbSI) should be larger than the one in SbSeI. These gaps
are shown in the total densities of states in Fig. 3.

The small arrows in Fig. 2 show the location of secondary minima
in the lowest conduction band. SbSI, in which microwave oscillations
have already been observed,[6] shows two minima, one at 0.25 eV and

another at 0.55 eV above the conduction band minimum at S. The

first is roughly midway along the ΓX symmetry line, and the second

is about midway along the ΓZ line. In SbSBr, there are also two

secondary minima, located in roughly the same locations as in SbSI.

In the lowest SbSeI conduction band there is one second minima,

midway between Γ and Z.

The existence of secondary minima in the lowest conduction band

of semiconductors is certainly no guarantee of the existence of

the Gunn effect. These minima, however, are an essential first

requirement, and the present band structures strongly suggest that

this requirement is met in the as-yet untested crystals of SbSBr and

SbSeI.

REFERENCES

1. Kirkuchi, A., Oka, Y. and Sawaguchi, E., J. Phys. Soc. Japan, 23, 337 (1967); Pikka, T.A. and Fridkin, V.M., Fiz. Tverd. Tela, 10, 2668 (1969); Furman, E. and Brafman, O. and Makovsky, J., Phys. Rev. B8, 2341 (1973).

2. Bercha, D.M., Slivka, V. Yu, Sybru, N.N., Turganitsa, I.D. and Chepur, D.V., Fiz. Tverd, Tela 13, 276 (1971). Trans. Sov. Phys.-- Solid State, 13, 217 (1971).

3. Berlincourt, D., Jaffe, H., Merz, W. and Nitsche, R., Appl. Phys. Lett. 4, 61 (1964).

4. Haffle, H.G., Wachernig, H., Irslinger, C., Grisar, R. and Nitsche, R., Phys. Status Solidi 42, 531 (1970).

5. Fridkin, V.M., Grekov, A.A., Rodin, A.I., Savchenko, E.A., and Volk, T.R., Ferroelectrics, Vol. 6, pp. 71-82, (1973); Belotskii, D.P., Gavrilenko, N.V., Katerinyuk, D.M., Kushnir, Ya. I., Lapshin, V.F. and Moik, I.B., trans. from Izvestiyq Akademii Nauk SSSR, Neorganicheskie Materialy, Vol. 9, 1142-1145, July 1973.

6. Sawaguchi, E. and Mori, T., J. Phys. Soc. Japan 21, 2077 (1966).

7. Cohen, M.L. and Heine, V., Solid State Phys. 24, 37 (1970); Alward, J.F., Perlov, C.M., Fong, C.Y. and Sridhar, C. Guha, Phys. Rev. B15, 5724 (1977).

8. Fong, C.Y., Petroff, Y., Kohn, S. and Shen, Y.R., Solid State Comm. 14, 681 (1974).

9. Wyckoff, R.W.G., Crystal Structure, Vol. 1, 2nd Ed., Interscience N.Y. (1963).

10. See Pikka and Fridkin, Ref. 1.

11. Shen, Y.R., private communication.

12. A preliminary SbSI charge density calculation reported at the Washington APS meeting in April, 1976, clearly showed that these states form a covalent bond with some of the Sb states. The remainder of the electrons of Sb atoms are transferred to the I atoms to form an ionic bond.

FIGURE CAPTIONS

FIGURE 1. Theoretical and experimental optical reflectivities of SbSI,
           SbSBr and SbSeI. Only the top four valence bands, and the
           bottom four conduction bands were used in the calculations.

FIGURE 2. Empirical pseudopotential band structures of SbSI, SbSBr
           and SbSeI. The smallest valence-to-conduction band gap
           is indicated by the long arrows in each band structure.
           The smaller arrows indicate the locations of second minima
           in the lowest conduction band.

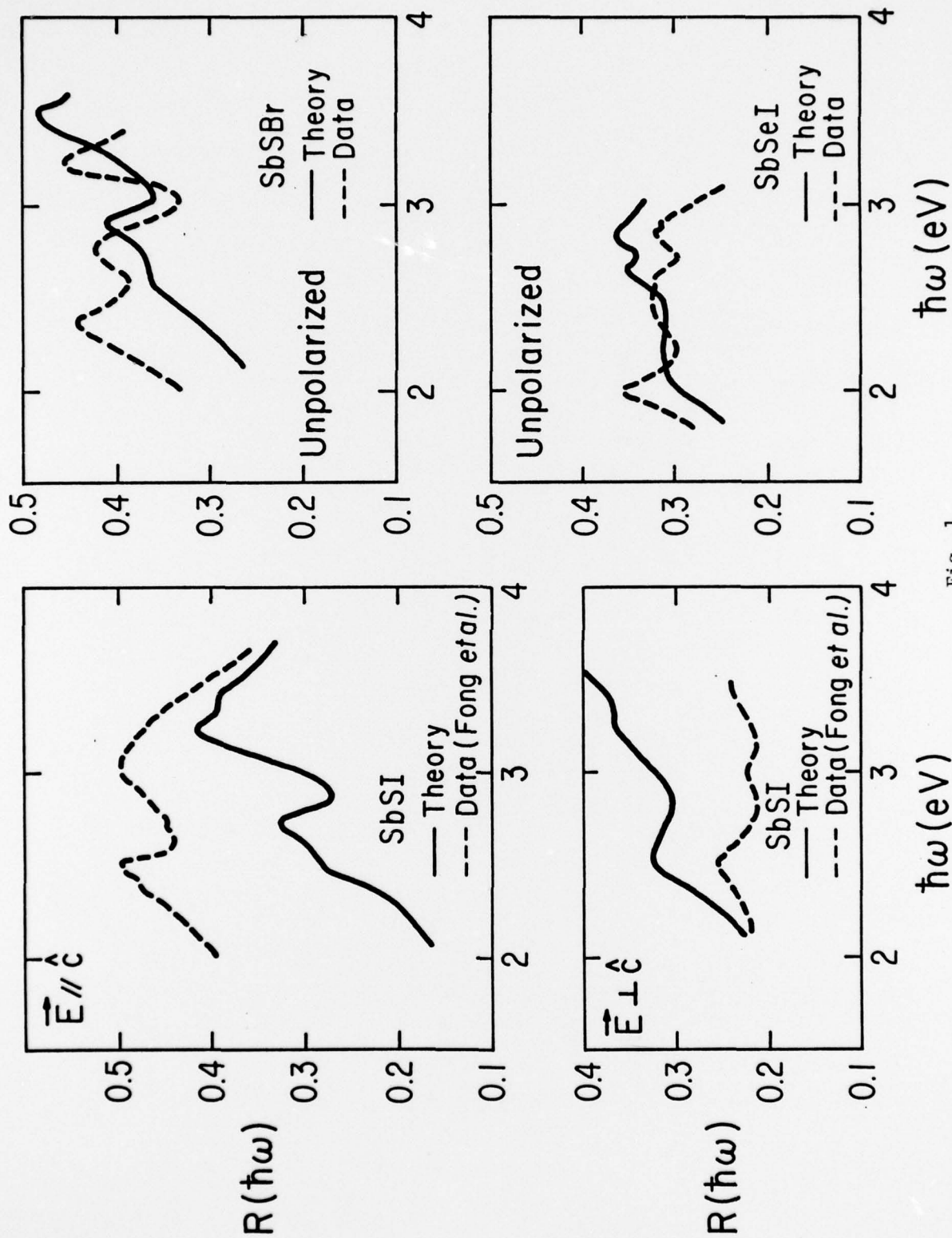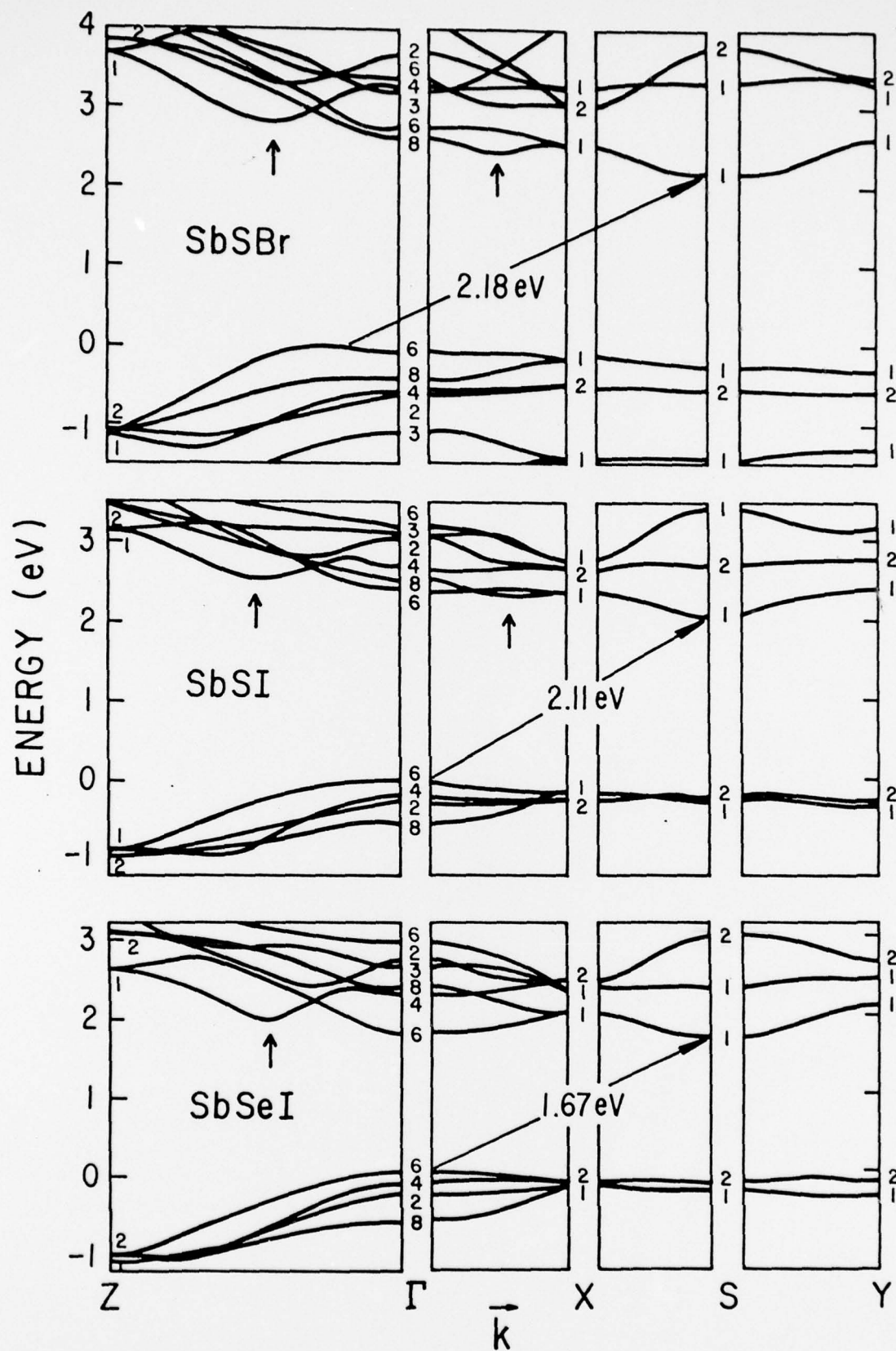FIGURE 3. The total densities of states of SbSI, SbSBr and SbSeI.
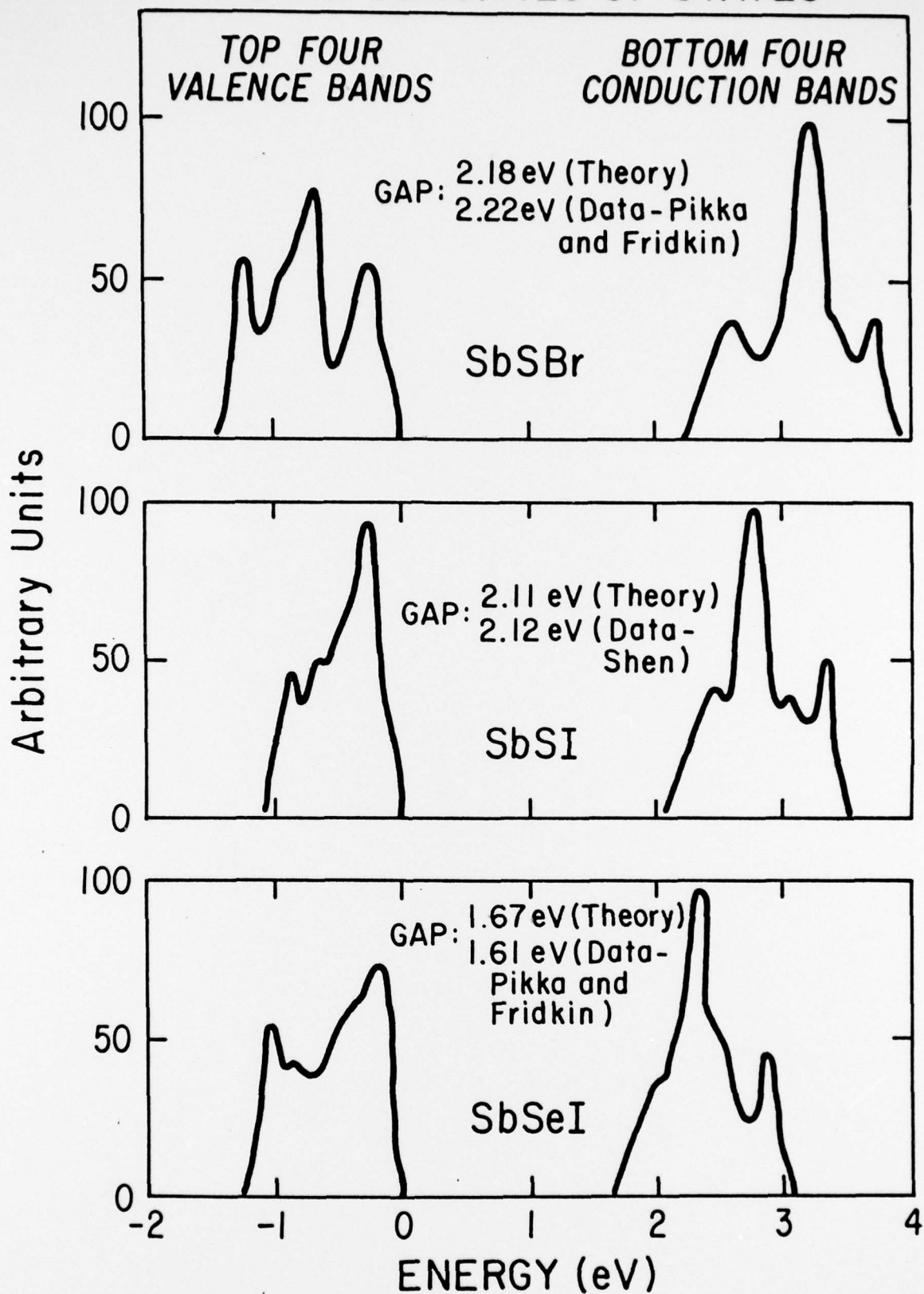
Fig. 1

Fig. 2

TOTAL DENSITIES OF STATES

Figure 3

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR- 78-0405	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Electronic and Optical Properties of SbSBr, SbSI and SbSeI.		5. TYPE OF REPORT & PERIOD COVERED Interim rept.
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) J.F. Alward, C.Y. Fong, M. El-Batanouny and F. Wooten		8. CONTRACT OR GRANT NUMBER(s) F49620-76-C-0016
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of California, Davis, CA 95616		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 2306/B2 61102F
11. CONTROLLING OFFICE NAME AND ADDRESS AFOSR-NE, Bolling Air Force Base Washington, D.C. 20332		12. REPORT DATE Oct. 1977
		13. NUMBER OF PAGES 12
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release, distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

SbSBr, SbSI, SbSeI, band structure, Raman Spectroscopy, reflectivity, Gunn effect, pseudopotential, ionic bond, density of states.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Electronic band structures of the ternary semiconductors SbSBr, and SbSeI have been obtained by using the empirical pseudopotential method (EPM) to fit our measured optical reflectivity data and earlier gap measurements. An SbSI band structure has been determined by fitting to earlier reflectivity and Raman spectroscopic data, and the results agree better with the data than do the results of an earlier preliminary EPM calculation. Above the SbSI conduction band minimum are secondary minima located midway along the $\Gamma 2$ and ΓX symmetry →

(over)

DD FORM 1473 1 JAN 73   EDITION OF 1 NOV 65 IS OBSOLETE

lines.   These minima may in part be responsible for the observed microwave oscillation (Gunn effect) in this crystal.   Similar minima in SbSBr and SbSeI are reported, suggesting these crystals might also show microwave properties.   The total densities of states are presented.